On the Adam-Gibbs-Wolynes scenario for the viscosity increase in glasses

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We reformulate the interpretation of the mean-field glass transition scenario for finite dimensional systems, proposed by Wolynes and collaborators. This allows us to establish clearly a temperature dependent length ξ^* above which the mean-field glass transition picture has to be modified. We argue in favor of the mosaic state introduced by Wolynes and collaborators, which leads to the Adam-Gibbs relation between the viscosity and configurational entropy of glass forming liquids. Our argument is a mixture of thermodynamics and kinetics, partly inspired by the Random Energy Model: small clusters of particles are thermodynamically frozen in low energy states, whereas large clusters are kinetically frozen by large activation energies. The relevant relaxation time is that of the smallest 'liquid' clusters. Some physical consequences are discussed.

I. INTRODUCTION

One of the most striking properties of 'fragile' glasses is the extremely fast rise of their viscosity η (or their structural relaxation time τ), that increases by 10 orders of magnitude as the temperature is decreased by less than a factor 2 [1]. The increase is faster than thermal Arrhenius activation over a constant energy barrier, and can be well-fit by the so-called Vogel-Fulcher (VF) equation [2]:

$$\log \eta = \log \eta_0 + \frac{\Delta}{T - T_{VF}}, \qquad (1)$$

at least in the range where the system can be equilibrated and the viscosity measured. Clearly, this becomes impossible when T approaches T_{VF}, and the above fit cannot be tested in the immediate vicinity of the predicted divergence. Correspondingly, other functional forms cannot be ruled out, such as a generalized VF form:

$$\log \eta = \log \eta_0 + \left(\frac{\Delta}{T - T_\gamma} \right)^\gamma. \qquad (2)$$

For example, many experimental results can also be reproduced with $\gamma = 2$, $T_\gamma = 0$ [3]. Many other functional forms have been proposed, see for example [4, 5], with equivalent goodness-of-fits. However, a rather remarkable aspect of the original Vogel-Fulcher equation is that the extrapolated freezing temperature T_{VF} is found to be very close, for a whole range of materials, to the Kauzmann temperature T_K where the extrapolated entropy of the glass becomes smaller than that of the crystal. More precisely, the ratio T_K/T_{VF} is in the range $0.9 - 1.1$ for a whole slew of glass formers, with T_K itself changing from

50 K to 1000 K – see [6]. This "coincidence" suggests that there might be some truth in the Vogel-Fulcher fit as well as in the extrapolation leading to T_K. It forcefully points towards an explanation of the viscosity increase in terms of a thermodynamic critical point, albeit of a non conventional type (for an interesting discussion of this point of view, see e.g. [7]). This perspective has attracted a great deal of attention over many years, starting from the early work of Adam, Gibbs and Di Marzio [8, 9, 10]. In particular, the theory of Adam and Gibbs predicts a relation between viscosity and configurational entropy of the glass $s_c(T)$ given by:

$$\log \eta = \log \eta_0 + \frac{\Delta}{T s_c(T)}. \qquad (3)$$

This relation is in rather good quantitative agreement with many experimental results [6, 10, 11, 12]. Qualitatively, the argument is that as the configurational entropy of the glass goes to zero, there are less and less available configurations to move the molecules around, and the dynamics slows down. However, the Adam-Gibbs theoretical argument is far from being water-tight, let alone convincing (see below). A related, but distinct, argument was proposed in the late 80's by Kirkpatrick, Thirumalai and Wolynes [13], and repeated (and partially reformulated) by Wolynes and collaborators in different contexts since then [14, 15, 16]. The basic ingredient of this theory is the nucleation of so-called 'entropic droplets' between different metastable configurations of the super-cooled liquid. Despite several quantitative successes reported in the literature [15, 16], it is fair to say that the entropic droplet scenario is still to convince many workers in the field. One of the reasons is that the physics behind 'the entropic driving force' leading to nucleation is rather obscure. The aim of this note is to propose a clearer – at least to our eyes – and somewhat different interpretation of the scenario of Wolynes et al. that leads to the Adam-Gibbs relation. A possible mechanism underlying the dramatic slow down of super-cooled liquids

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and the physical interpretation of the glass state appears clearly. Some semi-quantitative predictions of this picture are spelled out, and could be checked in numerical simulations and experiments.

II. THE ADAM-GIBBS AND WOLYNES ARGUMENTS REVISITED

Adam and Gibbs envision the super-cooled liquid as progressively organizing in larger and larger cooperative regions that have to collectively rearrange. Each of these cooperative regions, of linear size ξ, only has a few number Ω of preferred configurations, where Ω is independent of ξ – say $\Omega = 2$ (on this point, see [10]). The total entropy of the super-cooled liquid is therefore, for a volume V:

$$V s_c(T) = k_B \left(\frac{V}{\xi^3} \right) a^3 \log \Omega, \qquad (4)$$

where a^3 is the volume of a single molecule that we will set to $a = 1$ in the following. The next step is to *assume* that the energy barrier B for rearranging a region of size ξ scales with the total number of molecules in that region:

$$B = \Delta_0 \xi^3. \qquad (5)$$

Therefore, the time τ to collectively rearrange that region is given by:

$$\log \tau = \log \tau_0 + \frac{\Delta_0 \log \Omega}{T s_c(T)}. \qquad (6)$$

Identifying the viscosity and the relaxation time leads to the Adam-Gibbs relation Eq. (3) with $\Delta = \Delta_0 \log \Omega$. The difficulties in the above argument are that (a) it seems very unnatural to assume that the number of metastable configurations in a volume ξ^3 is independent of ξ. One would rather (see below) more naturally expect that this number is in fact exponential in ξ^3. (b) the barrier for rearranging a region of size ξ should scale as ξ^ψ with $\psi \leq d = 3$. The limit $\psi = d$ implies that the only possible relaxation mechanism is a cooperative movement involving *a finite fraction of all the particles*, which is unlikely for large ξ. In spite of these deficiencies, the Adam-Gibbs relation fares quite well in accounting for experimental data [6, 10, 11, 12], and the original Adam-Gibbs work has had (and still has) an enormous impact.

Another line of thought was initiated in a series of remarkable papers by Kirkpatrick, Thirumalai and Wolynes [13], that established a profound analogy between super-cooled liquids and the physics of a family of mean-field spin-glasses [17], which exhibit two transition temperatures. One is a dynamical transition temperature where (in mean-field) ergodicity is broken and the system is trapped close to metastable states of free-energy larger than that of the paramagnetic (liquid) state, which is still the thermodynamically stable state. This transition temperature can formally be identified with the Mode-Coupling transition (MCT) temperature T_{MCT} [13, 18]. The second transition, at a lower temperature T_0, corresponds to a *bona-fide* thermodynamical phase transition to a glassy phase, with no latent heat but a discontinuous order parameter (a transition called 'discontinuous' or 'random first order'). Between T_0 and T_{MCT}, the difference in free-energy between individual metastable states and the liquid state is found to be exactly the 'complexity', i.e. the log-degeneracy of the metastable states, that one can therefore associate to the configurational entropy of the liquid [63]. Roughly speaking, the total entropy of the liquid is made of a 'vibrational', bottom of valley contribution (that also exists, and is of similar magnitude, in the frozen glass or the solid phase), plus this configurational entropy that reflects the evolution of the liquid from one quasi-frozen configuration to another – an evolution that becomes impossible, in mean-field, when $T \leq T_{MCT}$. Since the configurational entropy vanishes continuously at T_0 in these mean-field models, it is tempting to associate T_0 with the Kauzmann temperature T_K. In finite dimensions, the mode coupling transition becomes a cross-over since barriers between metastable states are finite and some 'activated' dynamics still occurs below T_{MCT}. Furthermore, the thermodynamic ideal glass transition at T_K is avoided in many real cases (because of crystal nucleation for instance) but this turns out to be irrelevant for practical purposes [62] (see also the discussion in [13]). Wolynes and collaborators argue that the transitions between different states occur via nucleation [13], and that this process is responsible for the dramatic increase of the structural relaxation timescale. However, contrarily to usual nucleation where the driving force comes from a difference of bulk free-energy between the typical metastable state sampled at equilibrium and the invading phase, all metastable states here have the same bulk free-energy. The driving force is argued to be 'entropic', and given by the log-degeneracy of all *possible* phases; for a droplet of size ξ, the entropy gain would then be (in d dimensions) $-T s_c(T) \xi^d$, whereas the energy loss due to a mismatch between the nucleating phase and the surrounding state is given by a generalized surface tension $\Upsilon \xi^\theta$, with $\theta \leq d-1$. The two contributions balance when $\xi^{*(d-\theta)} = \Upsilon / T s_c(T)$. This length is interpreted [13, 14, 15] as the typical size of a 'mosaic' state, that pictures the super-cooled liquid as a patchwork of local metastable configurations. The free-energy barrier coming from the balance between the entropic driving force and the surface tension leads, through the Arrhenius relation, to a generalized Adam-Gibbs relation (in d dimensions):

$$\log \tau = \log \tau_0 + c \frac{\Upsilon}{k_B T} \left(\frac{\Upsilon}{T s_c(T)} \right)^{\frac{\theta}{d-\theta}}, \qquad (7)$$

where c is a model dependent constant. Using $s_c \sim T - T_K$, this corresponds to a generalized Vogel-Fulcher law, Eq. (2), with $\gamma = \theta/(d-\theta)$. It was argued in [13]

that $\theta = 3/2$ in three dimension and as a consequence one gets back to the usual Vogel-Fulcher and Adam-Gibbs laws. The obscure point of the above argument is the precise nature of the 'entropic driving force', in particular the way it mixes in a subtle manner static (thermodynamical) and dynamical considerations. Indeed, assuming the different cells of the mosaic state to be independent, the total entropy of the system is actually:

$$ \mathcal{S} = \frac{V}{\xi^d} s_c(T) \xi^d, \qquad (8) $$

which is independent of ξ, precisely because the entropy of each cell scales like ξ^d (at variance with the Adam-Gibbs picture, where it is independent of ξ). So, why should the system break up in different domains and pay surface tension? What exactly fixes the scale over which cooperative events take place? What is the physical meaning of the entropic driving force?

We believe that the picture of Wolynes et al. is in fact fundamentally correct, although the arguments supporting it are somewhat unsatisfactory. The aim of the following sections is to establish what we hope to be a more convincing version of these arguments. The following considerations actually share some similarities, but also important differences, with a very recent preprint by Lubchenko and Wolynes [20].

III. WHAT IS A GLASS ? A VIEW FROM THE RANDOM ENERGY MODEL

A. The glass transition in the Random Energy Model

A true glass has a solid-like response to shear and has thus an infinite viscosity. Since the viscosity is the integral over time of the stress correlation function, a glass is characterized by the fact that local stress fluctuations do not decorrelate in time. This is possible if the particles only visit, with appreciable probability, a finite number of configurations, a situation characteristic of *broken ergodicity* [21]. If all configurations can be probed with appreciable probabilities, then all correlation functions tend to zero in the long time limit: ergodicity is restored.

A simple, but illuminating model for such a behaviour is the Random Energy Model (REM), where the 2^N configurations have random, independent energies [22, 23]. For $T > T_K$, the entropy is non zero, which means that the system explores an exponential number (in N) of different states, each of which during a vanishing fraction of the total time. For $T < T_K$, on the other hand, the entropy is zero, and the system is localized in a finite number of configurations. More precisely, there are a finite number of configurations in which the system spends a finite fraction of the total time t_w, however long t_w might be [24, 25, 26]. At low temperatures, the energy dominates – even if there are 2^N states that await the system,

only the very low states have an appreciable probability to be occupied. As soon as T crosses the value T_K, however, the system is 'sucked up' by higher energy states because of their huge number. Because the number of visited states is finite for $T < T_K$, the system cannot forget its past, correlation functions do not decay to zero, one has a glass. For $T > T_K$, on the other hand, the system can lose itself in a large number of states, such that the probability to come back to an already visited state is close to naught. Autocorrelations then go to zero, the system is liquid. We shall show in the following that a similar mechanism is behind the existence of the mosaic state and fixes the length ξ, which actually plays the very same rôle as temperature in the Random Energy Model.

B. Entropy driven cluster melting

Consider a large ensemble of interacting particles that become glassy at low temperatures, for example a binary Lennard-Jones system or soft spheres, etc.. Let us assume that the liquid is trapped in one – call it α – of the (exponentially numerous) metastable states found in qualitative [13] and quantitative [27, 28, 29] mean-field-like studies. In the following we shall establish the length above which this assumption is inconsistent, providing an upper bound for the typical length-scale of the mosaic state. We freeze the motion of all particles outside a spherical region of radius ξ and focus on the thermodynamics of the small cluster of particles inside the sphere, $\mathcal{C}(\xi)$, subject to the boundary conditions imposed by the frozen particles outside the sphere. Because of the 'pinning' field imposed by these frozen particles, some configurations of $\mathcal{C}(\xi)$ are particularly favored energetically. When $\xi^d s_c$ is much larger than unity there are many metastable states for the particles in the cluster. Their number is

$$ \mathcal{N} \approx \exp[\xi^d s(f,T)/k_B] \qquad (9) $$

where f is the excess free energy per unit volume (counted from the ground state), and s the configurational entropy per unit volume at that free-energy. The boundary condition imposed by the external particles, frozen in state α, act as a random boundary field for all other metastable states except α itself, for which these boundary conditions perfectly match. As a consequence the partition function of the cluster $\mathcal{C}(\xi)$ is given by the sum of two contributions:

$$ Z(\xi,T) \approx \sum_{\beta \neq \alpha} \exp[-\xi^d \frac{f_\beta}{k_B T}] + \exp[-\xi^d \frac{f_\alpha}{k_B T} + \frac{\Upsilon \xi^\theta}{k_B T}] \approx $$
$$ \int_0^\infty df \exp\left[\frac{\xi^d \{Ts(f,T) - f\}}{k_B T}\right] + \exp\left[-\frac{\xi^d f_\alpha}{k_B T} + \frac{\Upsilon \xi^\theta}{k_B T}\right] (10) $$

where f_β is the excess free energy per unit volume that the state β would have with a typical, random boundary field created by another state, and the term $\Upsilon \xi^\theta$ is the

free energy gain due to the matching boundary condition (we have dropped the irrelevant factor $\exp(-\xi^d f_0/k_B T)$ where f_0 is the ground-state free energy). We focus on the case T close to T_K and study the stability against 'fragmentation' of a typical state α at that temperature, i.e. a state with excess free energy f^* equal to the one dominating the integral in (10), such that $ds/df^* = 1/T$. (States with a higher free-energy have very small probabilities to be observed at that temperature, and will typically not appear in the mosaic state. We will comment below on states with free energy lower than f^*). The partition function of the cluster immersed in the α state, $Z(\xi, T)$, then reads:

$$Z(\xi, T) \approx \exp[-\xi^d \frac{f^*}{k_B T}] \left(\exp[\xi^d \frac{s^*}{k_B}] + \exp[\frac{\Upsilon \xi^\theta}{k_B T}] \right). \tag{11}$$

The above expression is central to our argumentation. It is easy to see that when ξ is small enough, the second term, which is the contribution of the 'matched' state α, dominates the partition function, as long as $\theta < d$. On the contrary, the first term becomes overwhelming for larger ξ, and gives back exactly the free energy of the *liquid* state. Physically the system has the choice of either being in a single 'matched' state, losing configurational entropy but gaining the boundary free energy term, or being distributed over all the other states, thereby gaining the configurational entropy but losing the boundary term. In mean-field models, the entropy $s(f, T)$, as in the REM, vanishes linearly when $f \to 0$, with a negative curvature. This generically leads to an entropy s^* (and a free-energy f^*) that behave as $T - T_K$, in the vicinity of T_K. The cross-over between the two regimes therefore takes place for $(\xi^*)^{d-\theta} \propto \Upsilon/k_B(T - T_K)$. Assuming that energy barriers grow like ξ^ψ, one finds a typical equilibration time for the region $\mathcal{C}(\xi)$ given by:

$$\tau(\xi) \approx \tau_0 \exp\left(\frac{\Delta_0 \xi^\psi}{k_B T} \right). \tag{12}$$

For a frozen environment, the situation is therefore as follows: for small $\xi < \xi^*$, the dynamics from state to state is fast (low barriers) but leads to nowhere – the system ends up always visiting the same state. For larger $\xi > \xi^*$, the system can at last delocalize itself in phase space and kill correlations, but this takes an increasingly large time. *Thermodynamically*, large clusters are in the liquid state: see Eq. (11).

C. Relaxation times in the mosaic state

Since the hypothesis that the region $\mathcal{C}(\xi)$ is in the same state as its environment necessarily breaks down at ξ^*, it is reasonable to assume that this length-scale should be identified as the typical length-scale of the mosaic state. Note that a trivial lower bound for ξ^* is given by $s_c(T)^{-1/d}$, which coincides with the Adam-Gibbs prediction and comes from the fact that for smaller

length-scales there are typically no states available.

Thus, we came up with a scenario in which relaxation modes of length $\xi < \xi^*$ cannot be used to restore ergodicity in the system. The configurational entropy on these scales is too small to stir the configurations efficiently and win over the dynamically generated pinning field due to the environment. The motion on these length scales corresponds to a generalized 'cage' effect and contributes to the β-relaxation. Conversely, on scales $\xi > \xi^*$, the exploration of the different available states in nearby regions leads to a self-generated pinning field that decorrelates to zero, after a time scale $\sim \tau(\xi)$, i.e. ergodicity is restored by large scale modes $\xi > \xi^*$. From the above arguments, it is thus clear that the relaxation time is $\tau(\xi^*)$: smaller length scales are faster but unable to decorrelate, whereas larger scales are orders of magnitude slower so that the evolution on these scales will be short-circuited by a relaxation in parallel of smaller blobs of size ξ^*. Using $\xi^* \sim s_c^{1/(\theta-d)}$ and Eq. (12), we finally recover a result similar to Eq. (7) with the exponent $\theta/(d-\theta)$ replaced by $\psi/(d-\theta)$.

The values of θ and ψ should of course be calculated in the framework of a precise model. On general grounds one expects that they verify the inequalities $\theta \le d-1$ and $\theta \le \psi \le d-1$ [30]. If $\theta \le 0$ the system is at or below its lower critical dimension and the mean-field picture is completely wiped out. Since ξ^* is not expected to be much larger than $\sim 6 - 20$ in physical situations, these exponents are anyway not very accurately defined. Furthermore, as discussed in [16], the surface tension Υ is expected to vanish at T_{MCT} since at that temperature the metastable states become marginally stable. As a consequence, Υ increases from zero to a finite value as the temperature decreases from T_{MCT} to T_K. This leads, for the region of experimental interest where T is somewhat larger than T_K, to an effective exponent γ larger than the 'true' one in the immediate vicinity of T_K [62]. Finally, the value of $\gamma = \psi/(d-\theta)$ can vary quite a bit away from its Vogel-Fulcher value $\gamma = 1$ without changing dramatically the 'critical' temperature extrapolated from experimental data. For example, using $\gamma = 1/2$ would lead to a critical temperature only $5 - 10\%$ above the Vogel-Fulcher temperature, and would not strongly affect the near coincidence between T_γ and T_K.

The above argument gives the typical relaxation time in the system, relevant for example to compute the diffusion constant D of a tracer particle, expected to behave as $D \sim \xi^{*2}/\tau(\xi^*)$. On the other hand, the viscosity is proportional to the *average* relaxation time, which may in fact be dominated by the slowest regions in the system. This is related to the question of low energy states, with $0 \le f < f^*$, that we did not consider above. Repeating the above arguments, one finds that these states must fragment on a scale larger than ξ^*.

(More precisely, if $f = uf^*$, the scale ξ_u is given by $\xi^*/(u+\varepsilon)^{1/(d-\theta)}$ with $\varepsilon = (T-T_K)/T_K$.) The reason is quite simple: since they are (free-)energetically favored one has to reach a much larger size to balance the boundary free-energy term and the entropy gained by distributing the system over all the other states. What this implies is that there are, at any instant of time, regions of space corresponding to these low free-energy states that will be characterized by a somewhat larger length scales, but considerably larger relaxation times. While ξ^* is the typical length-scale of the mosaic state, we expect a distribution of length-scales up to a cut-off $\xi_{\max} \propto \xi^*/\varepsilon^{1/(d-\theta)}$, given by the fragmentation length of the lowest free-energy states [64]. Correspondingly, one has a very broad spectrum of relaxation times and strong dynamical heterogeneities: not surprisingly, the deepest states are slowest to fragment and relax. Since the ratio $\xi_{\max}/\xi^*$ diverges as $T \to T_K$, one finds that (a) the ratio of the average relaxation time $\langle\tau\rangle$ to the typical relaxation time $\tau(\xi^*)$ diverges as $T \to T_K$, accounting for the observed decoupling between viscosity and diffusion [31] and (b) the width of the distribution of the logarithm of relaxation times increases as the temperature is decreased, meaning that relaxation functions become more and more stretched as $T \to T_K$, again a common experimental observation. Within this framework, we also recover naturally the correlation between the stretching exponent β and fragility reported in [15].

Concluding this section, we note that the mechanism proposed in this section to relate the structural relaxation timescale to the behavior of the configurational entropy is different from the one of Adam-Gibbs. It is based, physically, on the competition between configurational entropy and dynamically generated pinning field. The very same competition induces a phase transition in the Random Energy Model. Although our argumentation is somewhat different from that of [20], it leads to very similar physical conclusions.

IV. REMARKS ON THE LENGTH ξ^* AND GENERALITY OF THE MOSAIC STATE

The conclusion of the previous section as well as the results of [13, 14, 15, 16] indicate that a system characterized by a discontinuous glass transition at the mean-field level has to be considered, in finite dimension, as a patchwork of local metastable states. It is important to remark that the length-scale ξ^*, which diverges at T_K, plays a different rôle than the usual correlation length close to a standard phase transition. In the latter case, the system appears critical on length-scales smaller than the correlation length whereas in the former case the system is mean-field like for $\xi < \xi^*$. From this perspective the liquid may also be considered as a patchwork of local mean field systems. This idea of 'blobs' is implicitly used in all energy landscape pictures for glassy dynamics (see e.g. [20, 32, 33, 34]). From the above discussion, these pictures certainly cannot describe the dynamics for time scales larger than $\tau(\xi^*)$.

We think that the mosaic picture is more general than originally proposed by Kirkpatrick, Thirumalai and Wolynes. As an example, consider the Kob-Andersen model [35, 36] which has a dynamical MCT-like transition at the mean-field level (actually on a random graph) and no transition but a very rapid increasing of the relaxation timescale in finite dimension. The dynamical MCT transition is due to the fact that at a certain density ρ_{MCT} an infinite cluster of completely blocked particle appears suddenly. As a consequence, for $\rho > \rho_{MCT}$, the configurational space is broken up in an exponential number of ergodic components, i.e. there is a finite configurational entropy [36]. In finite dimensions, this transition is destroyed: on length-scales larger than a (very rapidly increasing) length $\Xi(\rho)$ (see [36]) one finds with probability of order one some configurations of vacancies that can move cooperatively together. Instead, on lengths smaller than $\Xi(\rho)$ the system is completely jammed as for mean field systems in the regime $\rho > \rho_{MCT}$. Hence, in this case one also finds that the length $\Xi(\rho)$ separates a mean-field regime from a non mean-field one. Again, the liquid can be considered as a patchwork of local (mean-field like) metastable states. However, there are two important differences with respect to the case discussed in the previous section. First, $\Xi(\rho)$ is not determined by the competition between energy and entropy. Instead what happens is that on length-scale smaller than $\Xi(\rho)$ the configurational space is typically broken up in disconnected pieces which only start being connected on length-scales of the order of $\Xi(\rho)$ by very rare paths. Second, in the case of the Kob-Andersen model as well as for many other kinetically constrained models [37] the relation between time and length is $\tau \propto \Xi^z$, to be contrasted to the exponentially activated one, Eq. (12).

We think that for many glass-forming liquids, at least the ones for which the temperature, not the density, is the important control parameter inducing the glass transition [38], it is more likely that the mechanism behind the increasing of the relaxation time is the one described in the previous section. However, for other systems like colloids, modeled by hard spheres systems, the mechanism may be different and perhaps similar to the one discussed for the Kob-Andersen model [35, 36] and present in other Kinetically Constrained Models [37, 39]. In general, one expects a mixed scenario where both mechanisms interact to various degrees, with entropic and energetic slowing down entangled (see e. g. [40] for a toy model).

V. DISCUSSION AND CONCLUSION

The picture proposed in this paper seems to us to be the correct way to interpret for real systems the glass transition scenario suggested by mean-field models (which should be relevant for physical systems where temperature is the relevant parameter governing the glass transition [38]). Analytical calculations based on this approach [41] should allow one to obtain quantitatively the length ξ^* for a given glass-forming liquid, and complement the finite dimensional thermodynamic calculations of [27, 28, 29]. This would then put on a firmer basis the explanation of the glass transition first proposed by Kirkpatrick, Thirumalai and Wolynes [13]. In this scenario, the mode-coupling transition temperature T_{MCT} corresponds to the appearance of long-lived metastable configurations, which would be stable for infinite range interactions. Above T_{MCT}, these (typical equilibrium) states are not even locally stable, much as for spinodal points [13]. Below T_{MCT}, these metastable states are mutually accessible, but on a small length-scale ξ only a few are relevant, as in the Random Energy Model below its glass transition. The length-scale ξ actually plays the rôle of the temperature in the Random Energy Model; on lengthscales $\xi > \xi^*$ the system is in its liquid phase. Our argument above is a mixture of thermodynamics and kinetics: small systems are thermodynamically frozen in low energy states, whereas large systems are kinetically frozen by large activation energies. The relevant relaxation time is that of the smallest 'liquid' clusters. Mean-field energy landscape pictures that emphasize the importance of saddles and valleys/traps – see, e.g. [17, 24, 32, 33, 34, 40, 42, 43, 44, 45] – can at best be valid for time scales smaller than this relaxation time, i.e. for $\xi < \xi^*$. Interestingly, however, this includes the aging regime (where by definition) the waiting time t_w is smaller than $\tau(\xi^*)$), for which one may expect a short time regime where mean-field dynamics [17] is correct, before an intermittent, trap-like dynamics takes over. For times greater than $\tau(\xi^*)$, the 'cluster melting' mechanism discussed here sets in.

Let us emphasize that we have clearly identified a length ξ^* beyond which the mean-field picture is not consistent. If $\theta > 0$ the mean-field picture should still be a good starting point to describe the physics. The idea of a mosaic state seems to be the natural way to adopt the mean-field picture in finite dimensions. If instead $\theta \leq 0$, the mean field scenario is completely destroyed, much as for Ising spin systems for example where $\theta > 0$ only if $d > 1$. Thus, a natural question is the value of θ for glass-forming liquids, but also for all the other systems (pure or disordered, classical or quantum) for which a mean field glassy phase has been found [17]. It would therefore be very important to compute θ in finite dimensions for these models.

A way to try to extract numerically the value of the interface exponent θ for glass-forming liquids and test the mosaic picture would be to simulate the thermodynamics of small clusters embedded in a frozen environment chosen to be a typical equilibrium configuration of a larger sample. Our prediction is that the non ergodicity parameter (height of the plateau of any generic density correlation function) will be large for small ξ and decay rather abruptly to zero beyond ξ^*, signaling the dominance of configurational entropy effects. (See [46, 47] for simulations on glass-forming liquids analyzing similar effects; note however that these simulations access mainly the regime $T > T_{MCT}$ where, within the above framework, $\Upsilon = 0$ and the relevant dynamical lengthscale is the one associated to the MCT transition [48] rather than ξ^*. Further work would be certainly valuable to conclude whether $\theta > 0$ or $\theta < 0$.) This crossover scale ξ^* should increase when the temperature is decreased, and the relaxation time of the system should grow as an exponential of this cross-over scale ξ^*. The picture promoted here also suggests that the so-called β relaxation regime should exhibit non trivial scalings for $T < T_{MCT}$ since it involves motion on all scales $1 \leq \xi \leq \xi^*$. The prediction of a non trivial structure of the β relaxation in the super-cooled regime $T > T_{MCT}$ [18] is in fact a spectacular success of Mode Coupling Theory; it was in fact recently shown that the nature of the β relaxation in the vicinity of T_{MCT} involves the divergence of a dynamical length scale [48]. Finally, dynamical heterogeneities appear very naturally within this scenario, first in the MCT regime [48] and at lower temperatures because of the distribution of local free-energies within the mosaic.

We should also compare the above configurational entropy scenario with other recent proposals. Kivelson, Tarjus and others [4] have argued that the slowing down of the dynamics is associated to the proximity of an avoided second order phase transition. Although the local order parameter of this phase transition is not easy to define and measure, the existence of a supra-molecular length scale comes from the incipient order that is trying to grow below the the avoided transition temperature. Although the underlying physics is rather different from the above scenario, a great deal of the phenomenology is expected to be rather similar. In particular, the system is expected to be frozen (ordered) on short scales and 'paramagnetic' (liquid) beyond a certain length scale.

Another suggestion is that the slow dynamics is governed by the rarefaction of 'mobility defects', i.e. simple defects that unlock the dynamics in their immediate vicinity. This idea dates back to Glarum [49] in the '60s, and was revisited within the context of kinetically constrained models by Fredrickson and Andersen [50]. This picture has been actively promoted in a series of recent papers by Garrahan, Chandler and collaborators [5, 51, 52] (cf. also the discussion in the previous section

and the review [37]). Although these models lead to dynamics that differ in their details, they all posit a complete decoupling between thermodynamics and kinetics, leading to a 'non topographic' scenario for the glass transition [5], in sharp contrast with the potential energy landscape and configurational entropy ideas. Thus, these models have nothing to say on the observed Adam-Gibbs correlations between configurational entropy and kinetics, which can only be accidental from their point of view. Roughly speaking the characteristic length scale ξ^* is in this case the typical distance between these rare defects. A small cluster of size $\xi < \xi^*$ typically contains zero defects and is kinetically frozen, except for small probability instances where it is fluid. For $\xi > \xi^*$, the defects present allow the system to relax on a time scale that behaves as a power-law ξ^{*z}, rather than an exponential (zero dimensional defects correspond formally to $\psi = 0$). This is an important quantitative and qualitative difference with an activated barrier scenario: in order to have very large times (as it is the case close to the glass transition) one needs very large length-scales. For instance, in order to reach relaxation times 10^{12} larger than the microscopic time, ξ^* has to be quite large – for example, for $z \approx 4$ [52], one obtains a ξ^* of the order of thousand diameters of particles, much larger than in a barrier dominated scenario. Another important difference is the structure of the β relaxation, which is expected to be rather trivial in these models. Let us note, however, that for other models not characterized by simple diffusing defects, like the East model, the exponent z increases upon lowering T and therefore more modest length-scales are needed

to produce a change of twelve order of magnitude in the timescale [51]. Furthermore the β relaxation also turns out to be non trivial in these models [53]. The fundamental difference with the mosaic state picture will then be in the dimensionality of the cooperative regions and, correspondingly, on the order of magnitude of the configurational entropy per particle at the glass transition – small for diluted defect models and of order k_B for the mosaic state [20].

We hope that a clear distinction between these pictures will emerge in the near future, thanks to the combined efforts of experiments, numerical simulations and theoretical arguments to define and measure dynamical lengths in glassy systems [16, 48, 51, 52, 54, 55, 56, 57, 58, 59]. From a theoretical point of view, it is extremely important to substantiate the claims made above by detailed calculations in the context of a specific model [41]. Models with long-ranged, Kac like interactions look promising in this respect [60, 61].

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[63] Depending on the author, the meaning of configurational entropy appears to be different. Here and in the following we call configurational entropy the logarithm of the number of metastable states. See [13, 19] for discussions.

[64] We assumed that the configurational entropy vanishes linearly in f and that $\partial S/\partial T \leq 0$ at least close to the lowest free-energy states